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This presentation is about cure characteristics of tricyanate ester high-temperature composite resins.

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CURE CHARACTERISTICS OF TRICYANATE ESTER HIGH-TEMPERATURE COMPOSITE RESINS

24 May 2011

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Outline

- Background
- Cure of Flexible Core Tricyanate Esters
  - Effect of Molecular Structure
  - Effect of Monomer Purity
  - Comparison of Measurement Techniques
    - Activation Energy
    - Conversion
- Conclusions

Acknowledgements: Air Force Office of Scientific Research, Air Force Research Laboratory – Program Support; Dr. Lawrence Baldwin (NAWCWD), thermal analysis, Dr. Thomas Groshens (NAWCWD), X-ray analysis; PWG team members (AFRL/RZSM)

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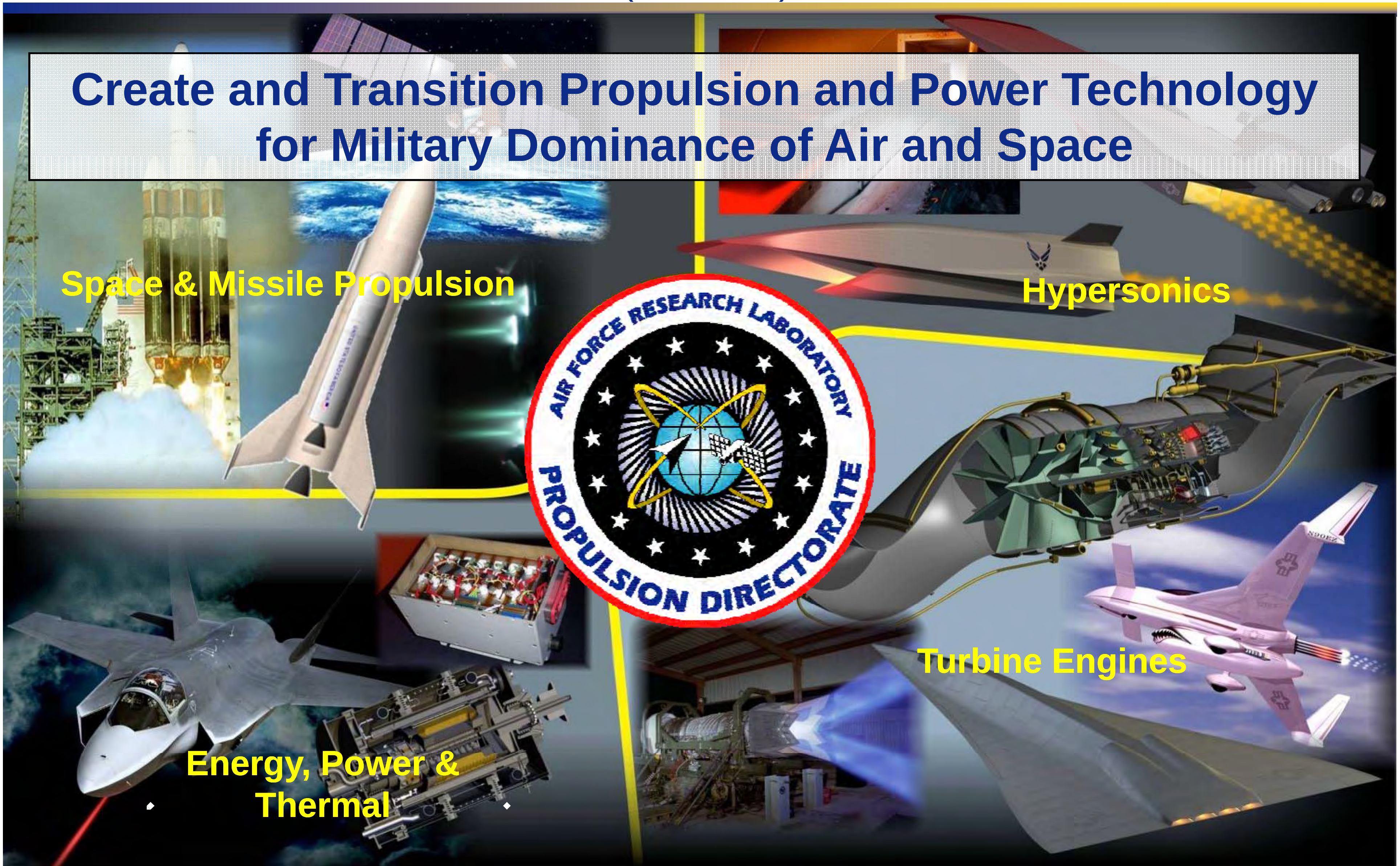

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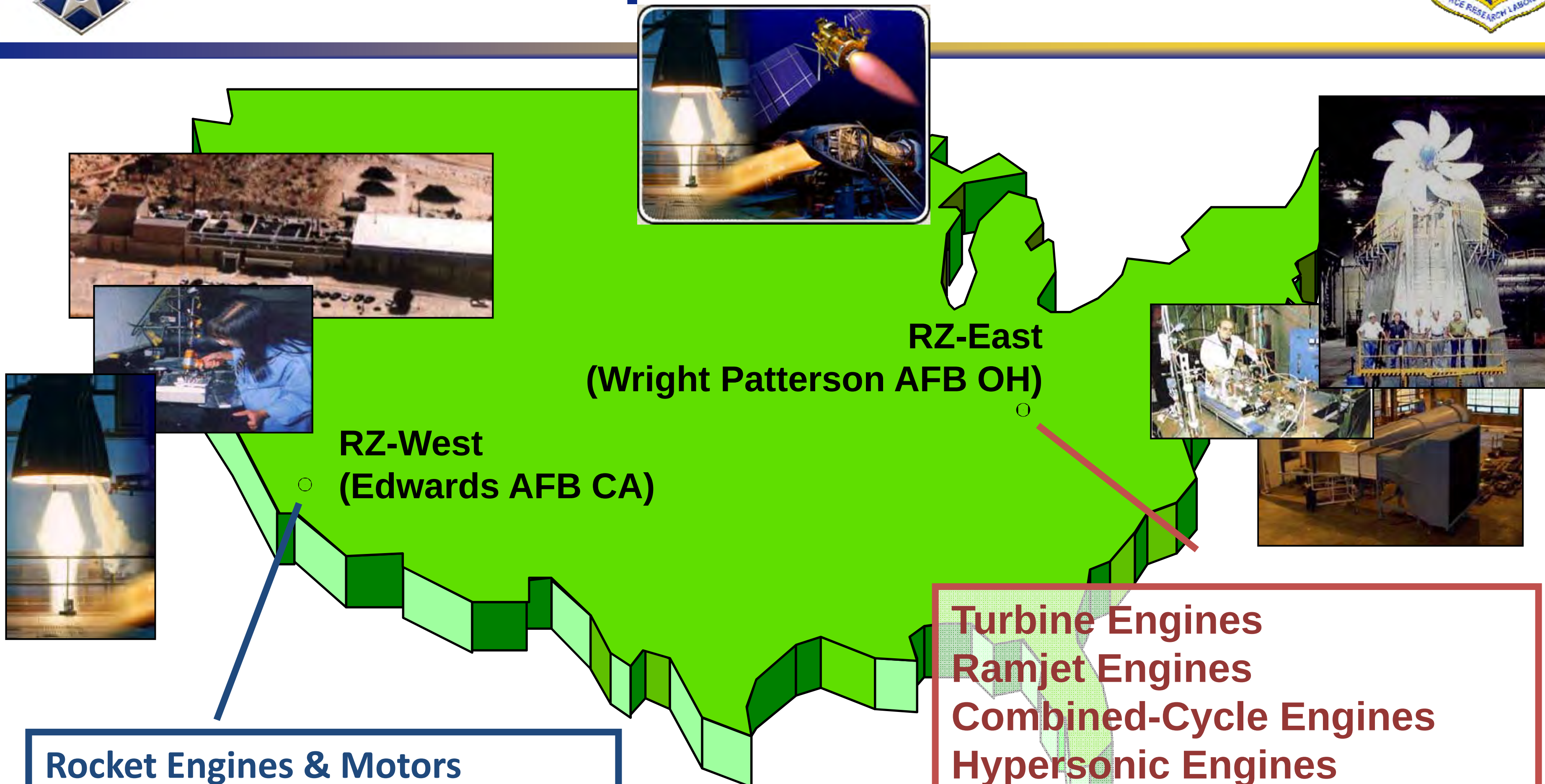

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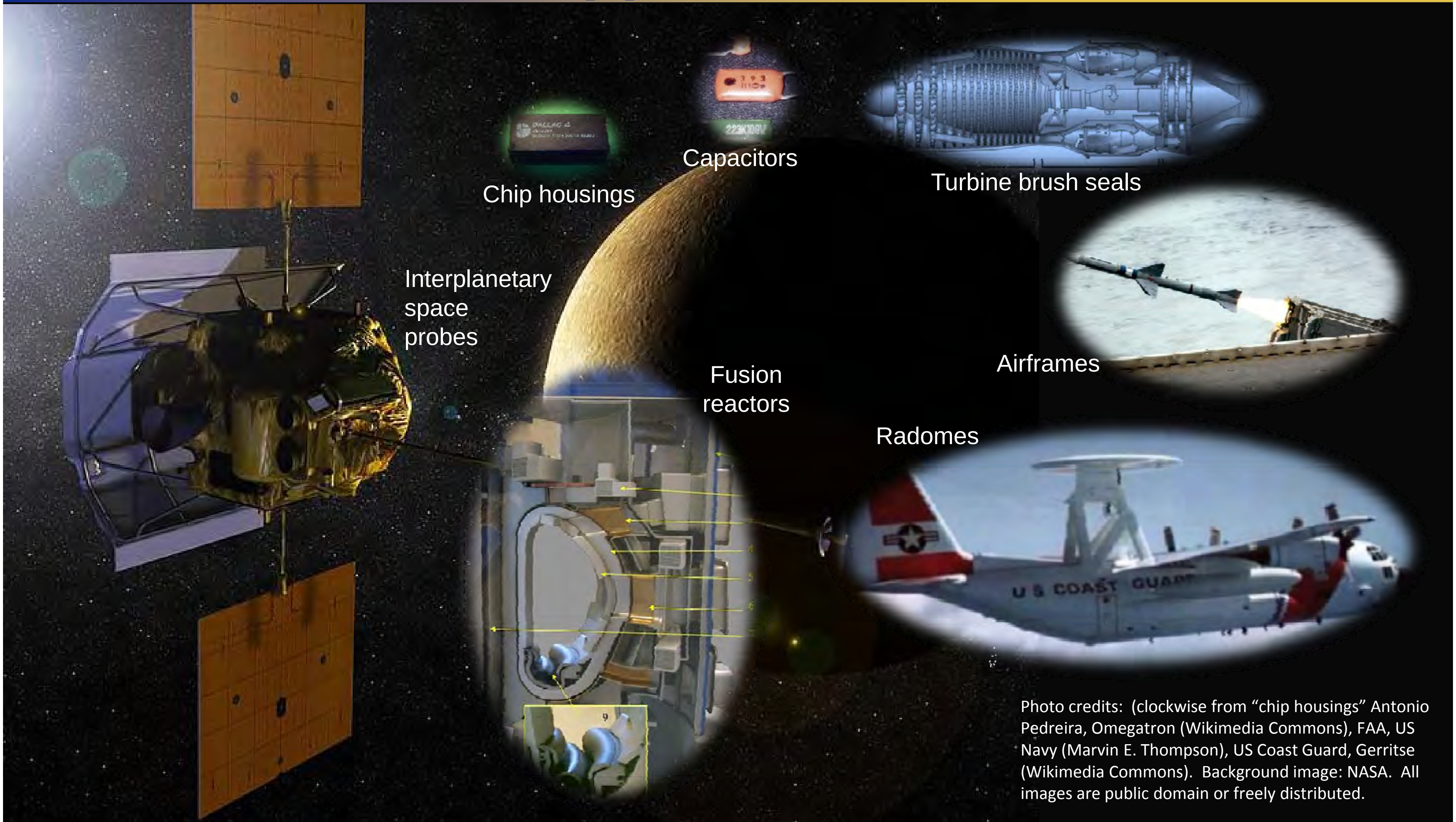
Thermal Management
Fuels and Propellants
System Analysis

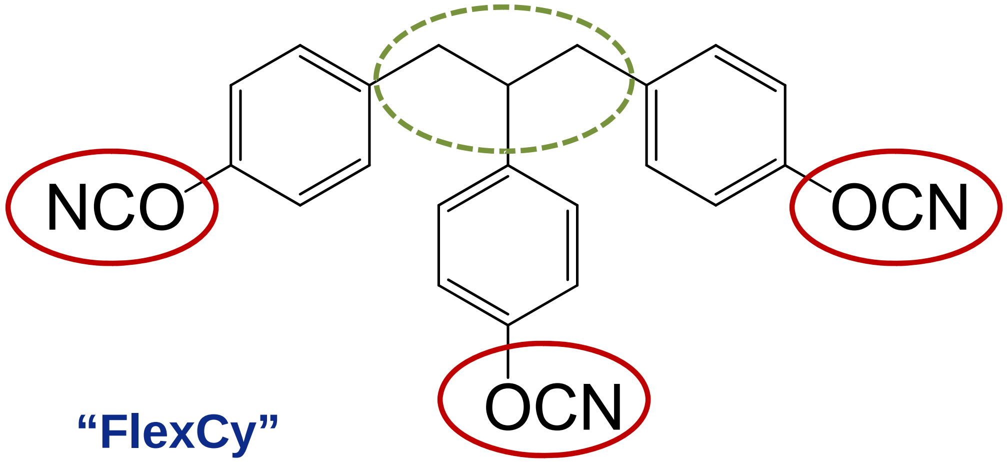
Cyanate Esters: Universe of Applications



- **Understanding cure kinetics is essential to fabricating items like these …**

Tricyanate Ester with Enhanced Molecular Flexibility

GOAL: Explore the effect of a "flexible core" architecture in overcoming limitations such as incomplete cure, brittleness, and severe drop in T_g under wet conditions associated with rigid high-T_g tricyanate esters.



"FlexCy"

AF/Navy Collaboration:

Monomer synthesized by Dr. Matthew Davis at NAWCWD China Lake

NAVAIR

Publications:

Guenthner, A. J.; Davis, M. C.; Lamison, K. R.; Yandek, G. R.; Cambrea, L. R.; Groshens, T. J.; Baldwin, L. R. , and Mabry, J. M. "Synthesis, Cure Kinetics, and Physical Properties of a New Tricyanate Ester with Enhanced Molecular Flexibility" *Polymer*, submitted (2011).

- Trifunctional architecture offers density of cyanate groups and aromatic content nearly equal to PT-30 for high dry Tg
- Flexible central branch point enhanced conformational degrees of freedom for more readily obtaining full cure

"Control" molecule: Primaset® PT-30

Types of Comparisons Performed

Molecular Structure

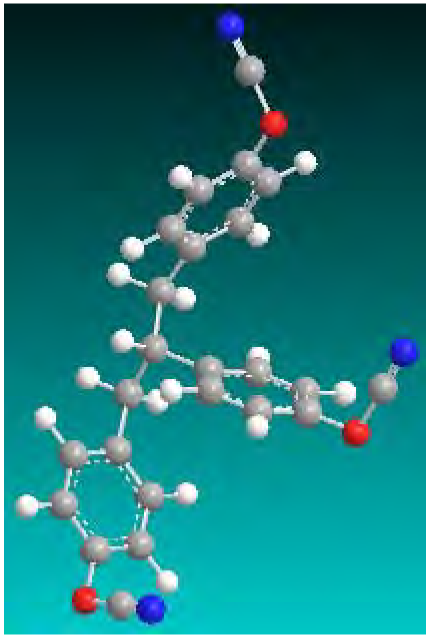
- FlexCy vs. Primaset® PT-30 (Lonza)

Methods of Purification

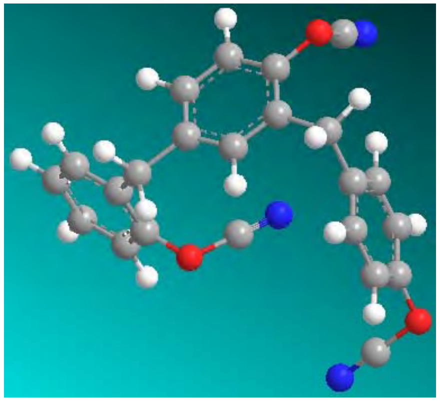
- Precipitated into ethanol (lower solubility results in higher yield but higher level of impurities)
- Precipitated into isopropanol (higher solubility lowers yield but is more effective at removing impurities)

Methods of Measurement

- Isothermal kinetics (rates and heat of reaction at one temperature; requires multiple experiments to measure activation energy)
- Non-isothermal kinetics (simpler, single experiment to measure activation energy and heat of reaction)

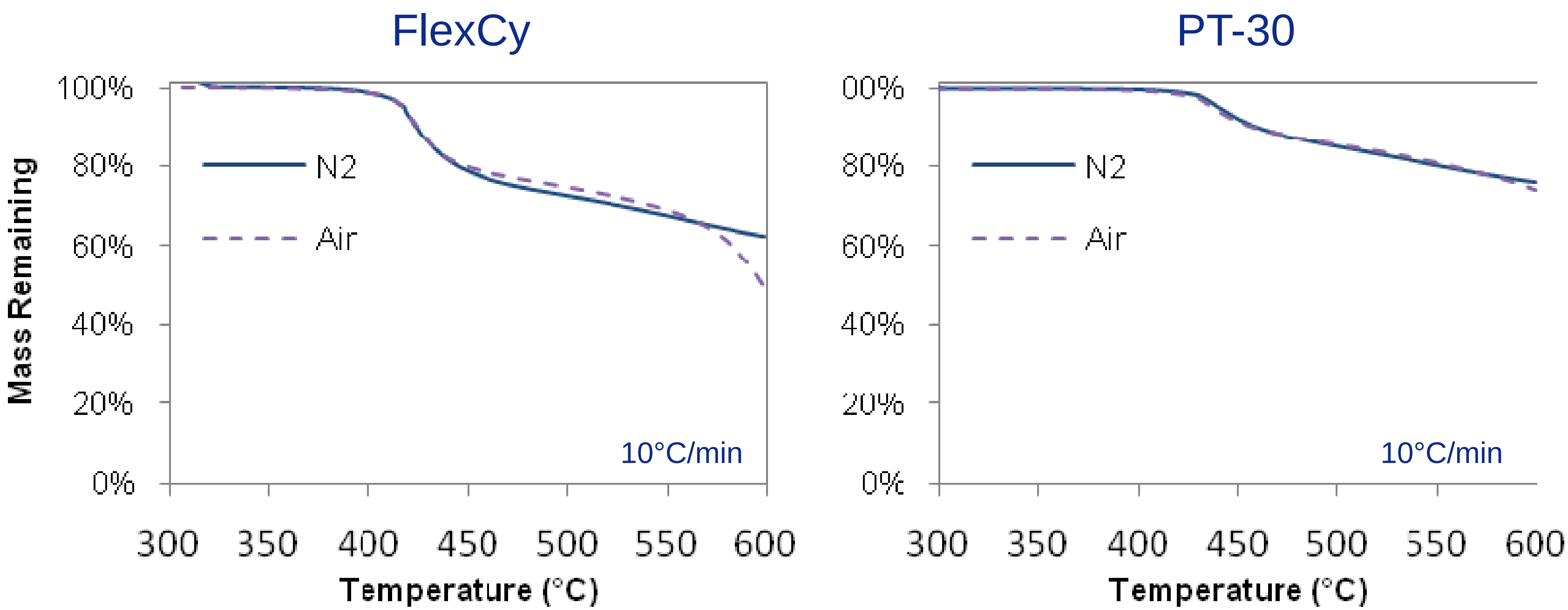


"FlexCy"



"PT-30"

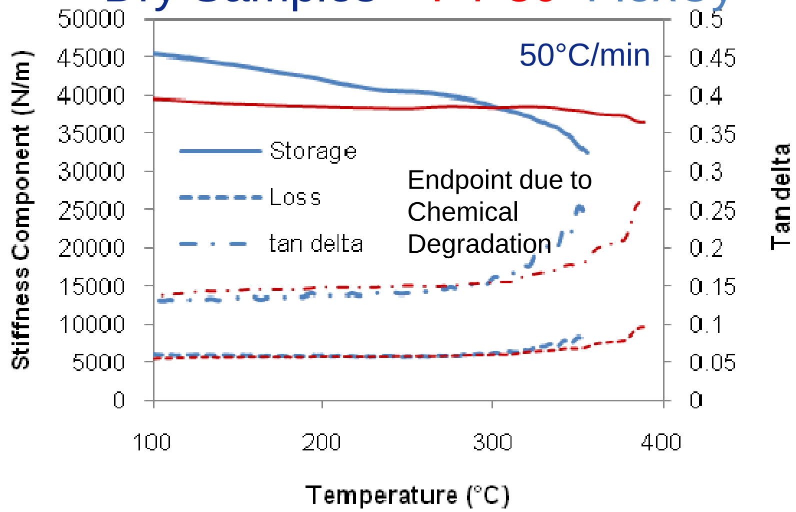
FlexCy and Primaset® PT-30: TGA Analysis



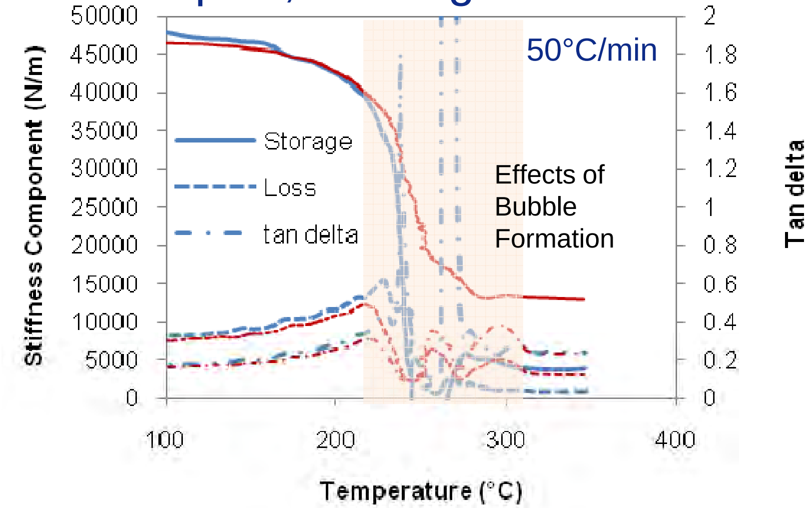
- FlexCy shows decreased thermal stability compared to Primaset® PT-30
- FlexCy thermal stability exceeds dicyanates for char yield and matches dicyanates for decomposition temperature.
- High char yields are a direct result of the high aromatic content in both FlexCy and PT-30

FlexCy and Primaset® PT-30: Dynamic TMA Data

Dry Samples – PT-30 FlexCy

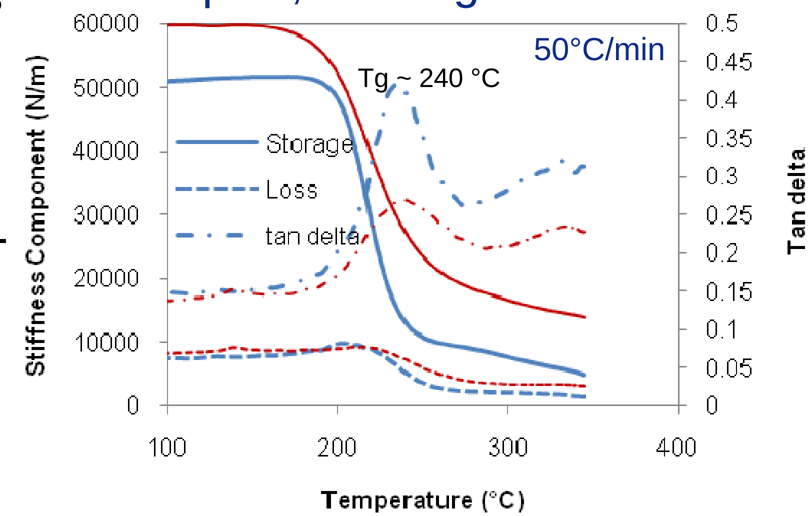


Wet Samples, Heating – PT-30 FlexCy

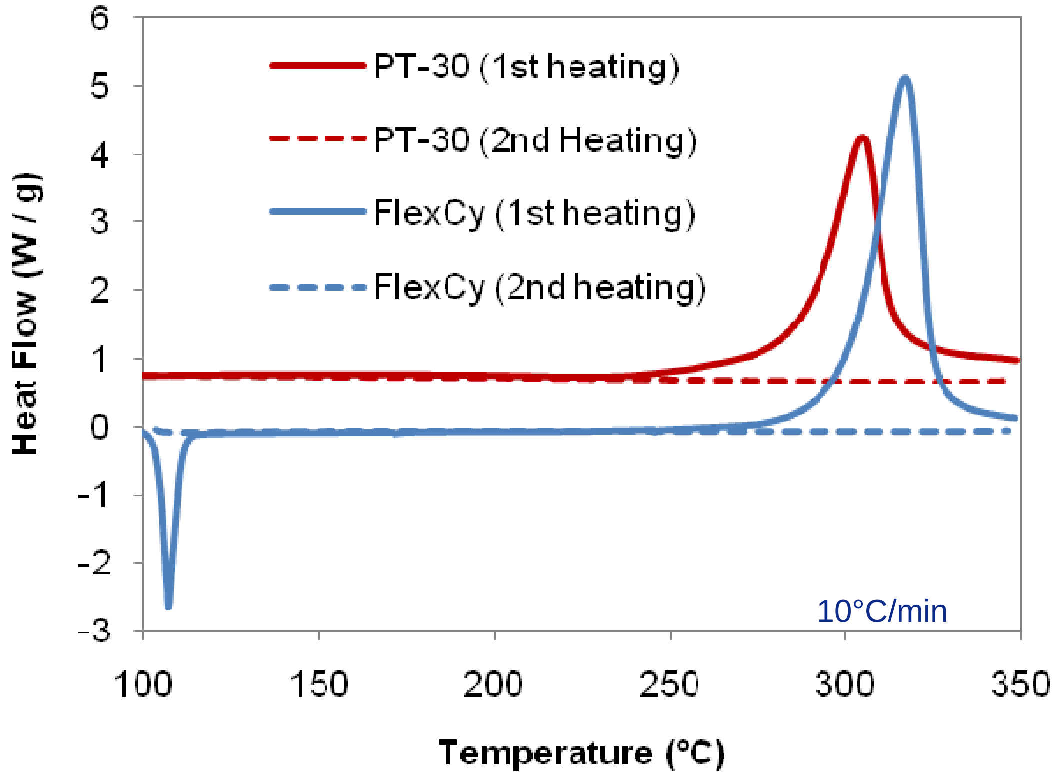


- PT-30 retains rigidity at higher temperatures when dry due to both thermochemical and thermomechanical effects.
- After exposure to 85 °C water for 96 hrs, both PT-30 and FlexCy have similar thermo-mechanical properties, with Tg ~ 240 °C.
- Bubble formation on rapid heating of wet samples is evident in both materials.

Wet Samples, Cooling – PT-30 FlexCy

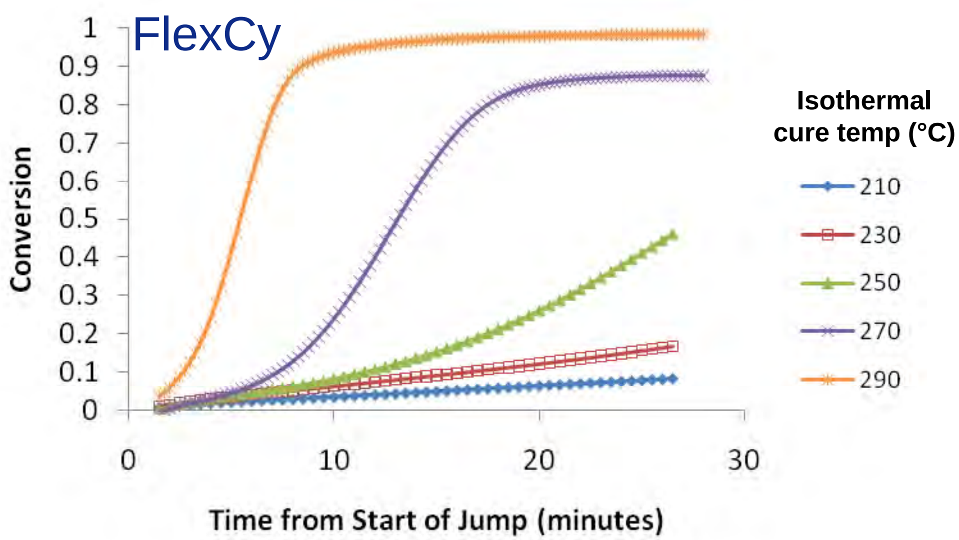


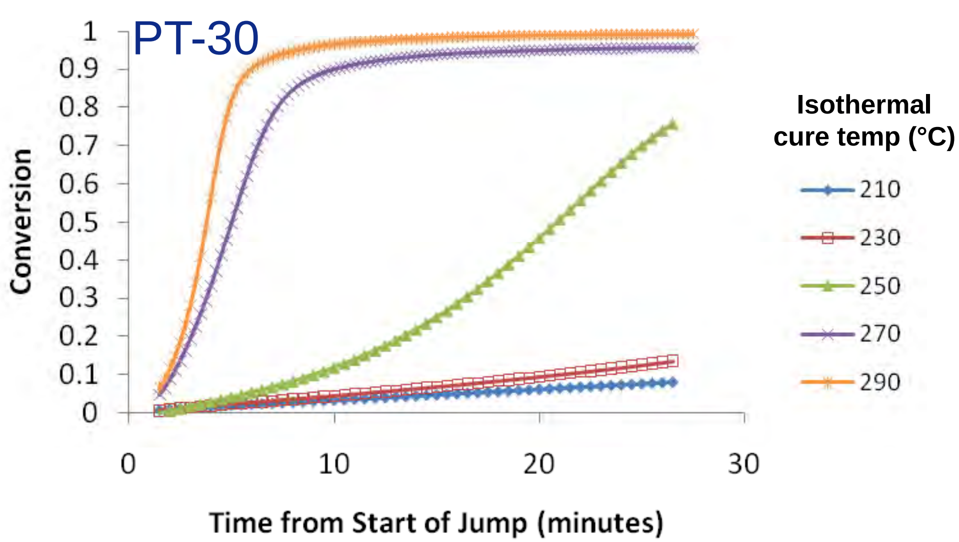
FlexCy and Primaset® PT-30: Initial DSC Analysis



- DSC shows both FlexCy and Primaset® PT-30 are of high purity (cure temperature exceeds 300 C)
- FlexCy has a slightly higher peak exotherm temperature and narrower exotherm due to lower impurity levels (not less favorable cure kinetics)

FlexCy and Primaset® PT-30: Isothermal Cure Kinetics

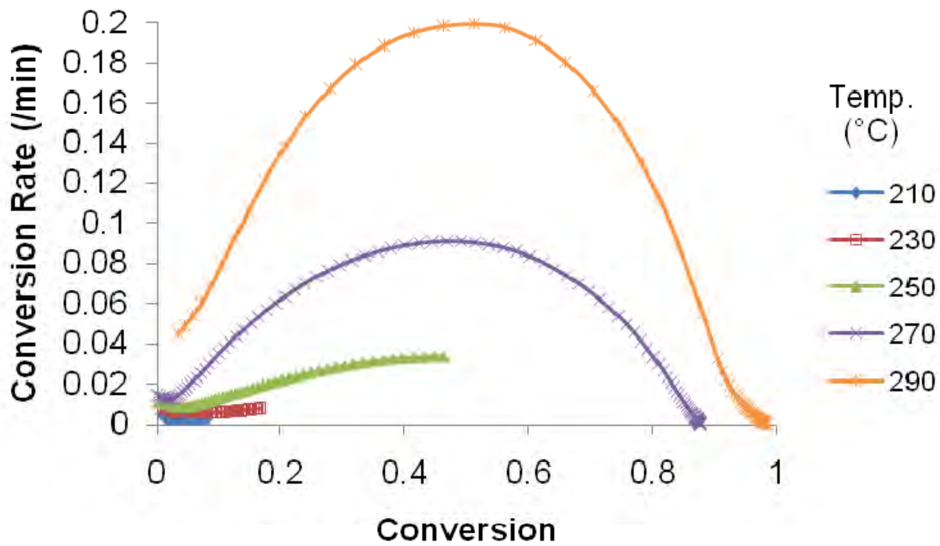


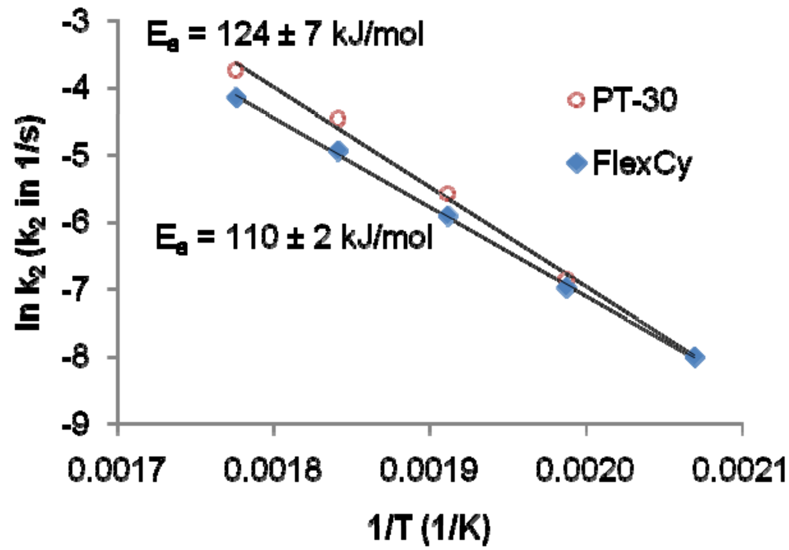


- Extent curves are calculated by integrating DSC isothermal heat flow data using constant baselines from post-cure (when available) or pre-cure isothermal holds.
- Note that extent of cure is based on measurement of residual exotherm by DSC on heating to 350 °C, thus the conversion numbers are not necessarily absolute.
- Heating and quench rates following 30 minute isothermal periods are approximately 100°C / min.
- Note that overall rates of cyanate ester cure are almost entirely the result of impurity levels; the temperature dependence is a more intrinsic feature.

FlexCy and Primaset® PT-30: Activation Energy for Cure

FlexCy Kinetic Data

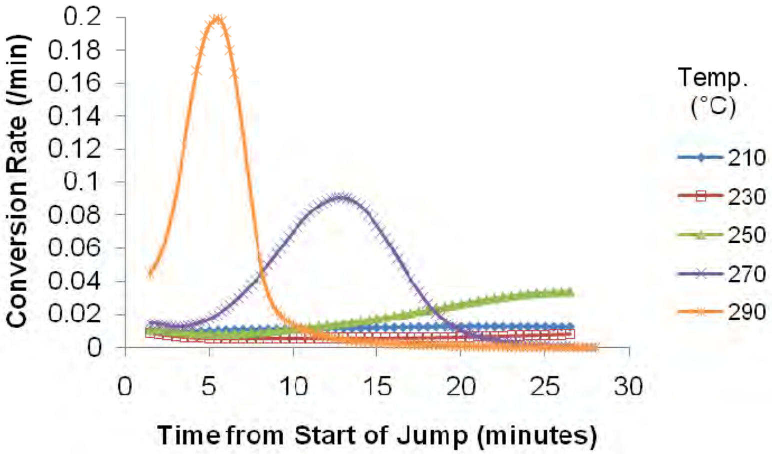


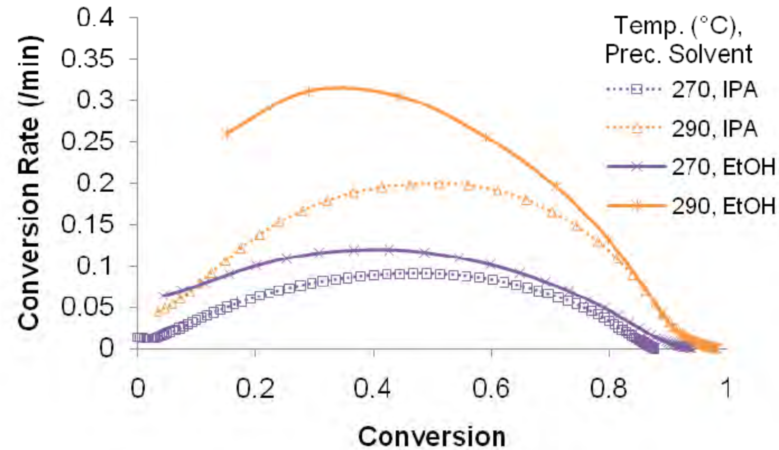


- Kinetics fitted to Kamal model: $d\alpha/dt = k_1 (1-\alpha)^n + k_2 \alpha^m (1-\alpha)^n$
- As expected for highly pure systems, k_2 (auto-catalytic) >> k_1 (catalytic), allowing for the simplification $\alpha|_{d\alpha/dt\text{-max}} = m / (m+n)$
- Activation energy computed based on k_2 value obtained by forcing constant m, n for all temperatures
- Lower activation energy for FlexCy is robust toward analytical assumptions
- Measured activation energies are similar to those reported for other cyanate esters (e.g. Simon, S. L. ; Gillham, J. K., J. *Appl. Polym. Sci*. **1993**, 47, 461).

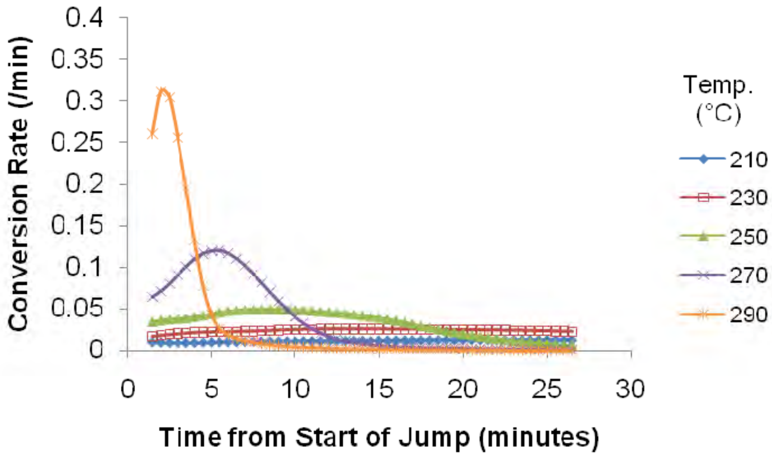
Effect of Purity on Cure Kinetics of FlexCy

Precipitated into IPA (higher purity)



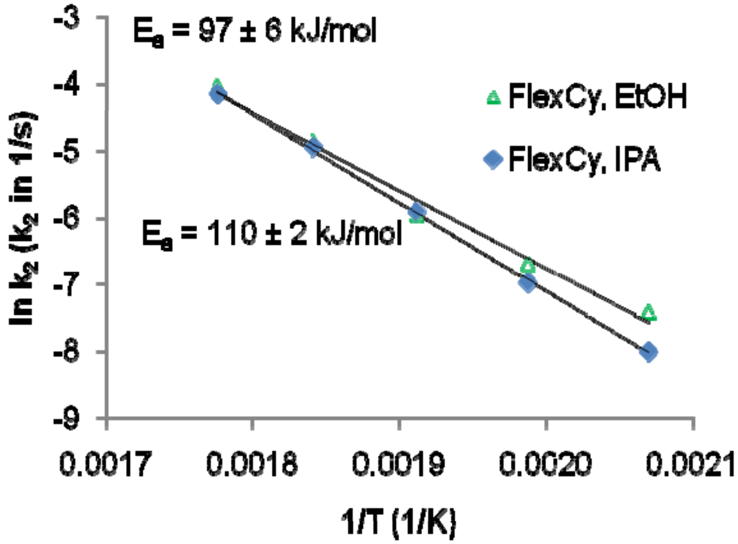


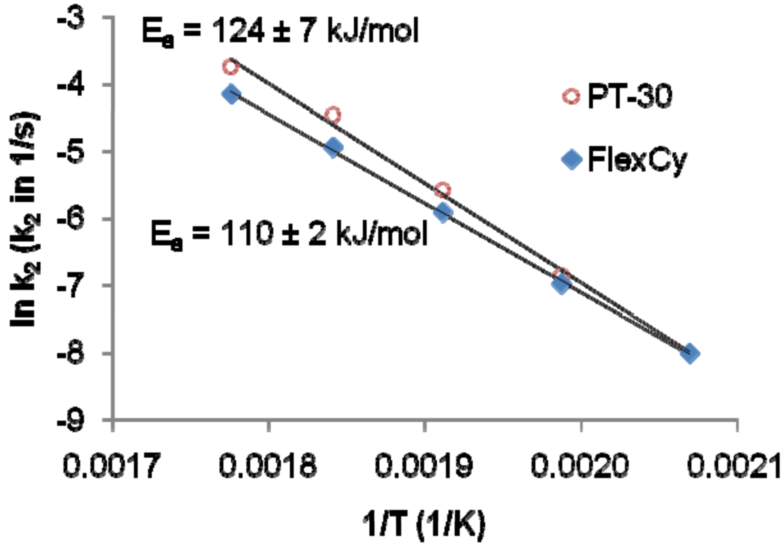
Precipitated into EtOH



- Increased impurities lead to more rapid cure and higher overall rates of cure.
- The effect takes place mainly at low conversions, indicating the difference is primarily in the k_1 parameter (catalytic) in the Kamal model.

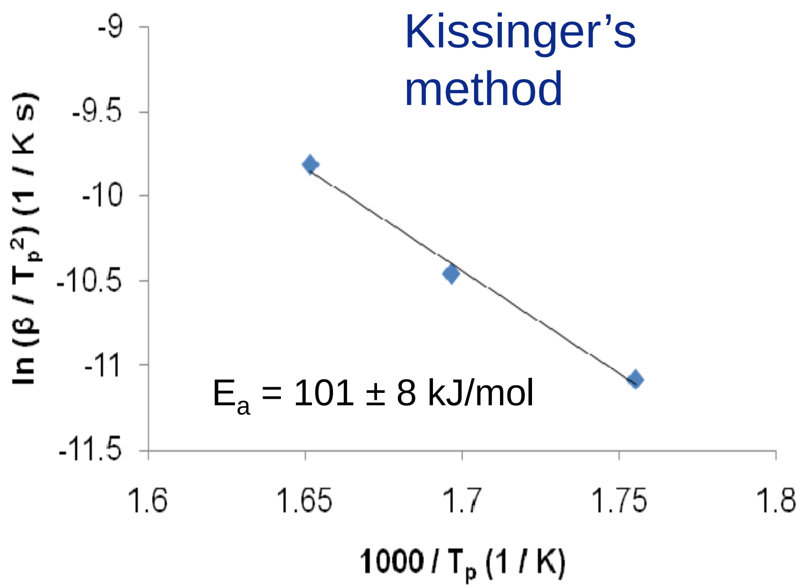
Effect of FlexCy Purity on Activation Energy

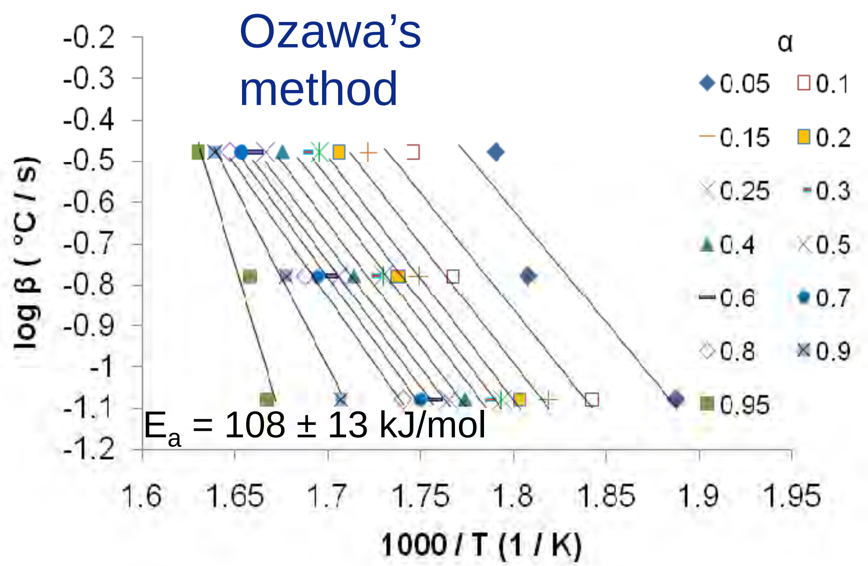


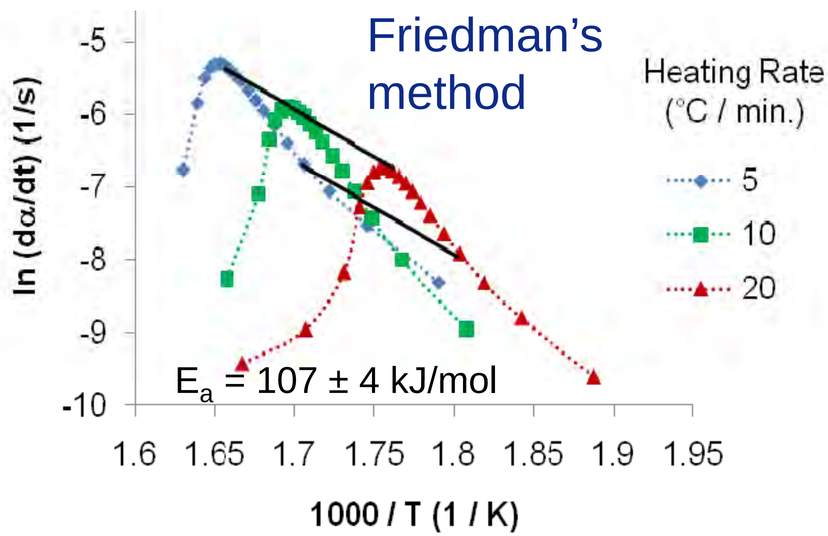


- Activation energy computed based on k_2 value obtained by forcing constant m, n for all temperatures
- Activation energies appear similar for all FlexCy samples above 230 °C, but appears to drop to ~80 kJ/mol at lower temperatures.
- The lower apparent activation energy at low temperatures may be the result of spurious attribution of catalyzed cure (dominant at these low temperatures) to the auto-catalytic route in the Kamal model.

Non-isothermal Cure Kinetics for FlexCy-IPA



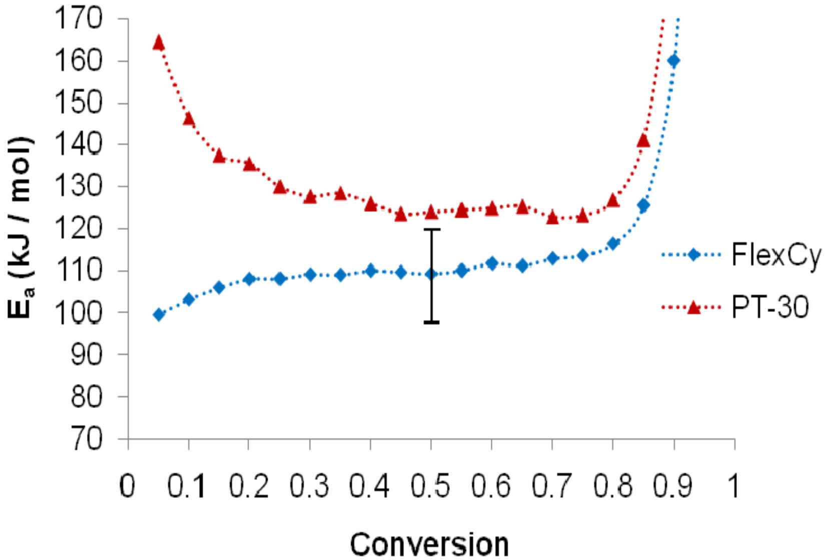




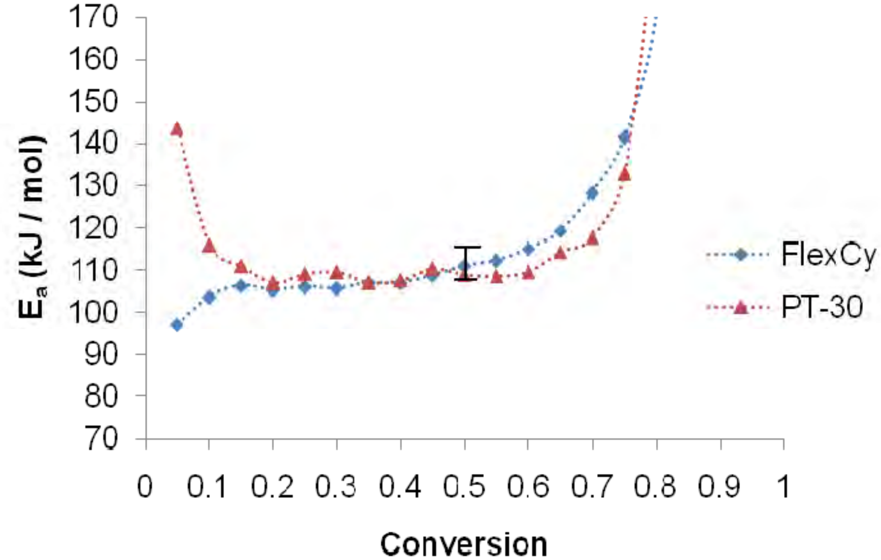
- The activation energies are all similar, and agree with the range of values (103 – 110 kJ/mol) found by four different versions of the isothermal method.
- Ozawa's method showed the greatest non-linearity but also the greatest consistency across conversions.

FlexCy and Primaset® PT-30: Non-isothermal Kinetics Compared

Ozawa's method



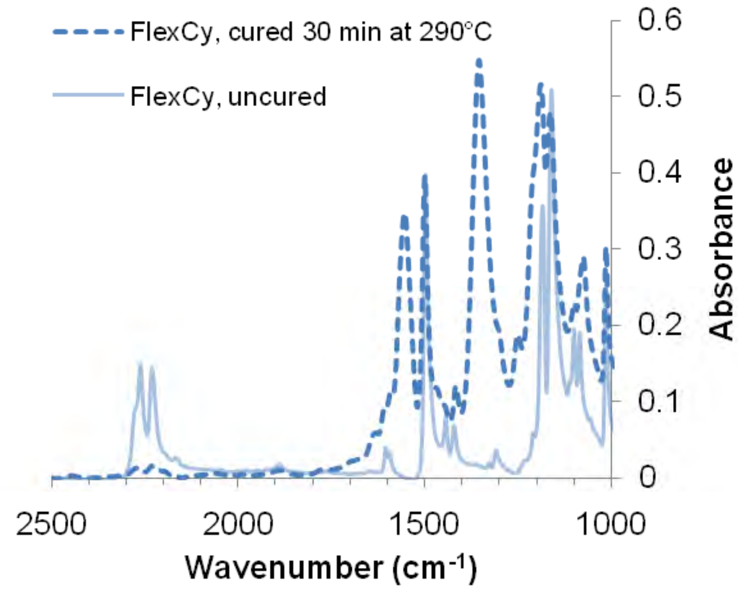
Friedman's method



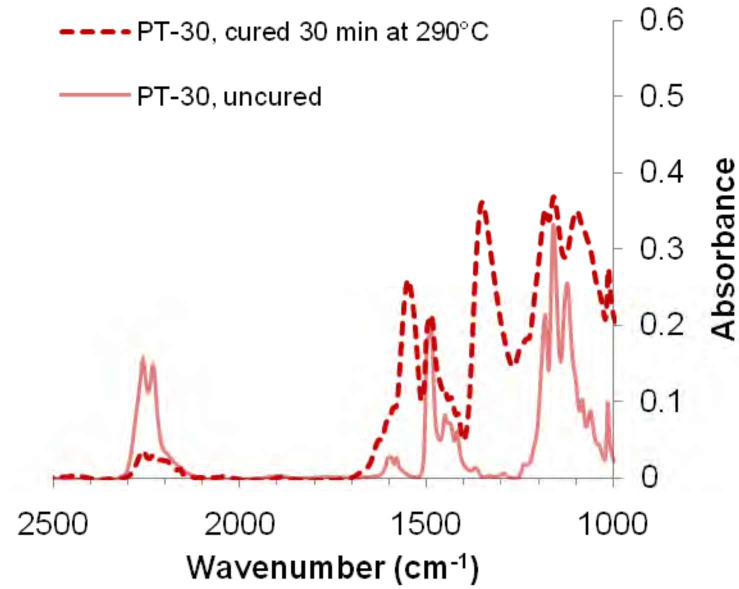
- Ozawa's method shows higher activation energy for PT-30 across all conversions, whereas Friedman's method shows significant differences only at low conversions due to an activation energy for PT-30 that is lower than all other methods
- Data at very low conversions is subject to large errors due to DSC baseline uncertainties and a low signal-to-noise ratio; the increase in activation energy at high conversions reflects gelation and vitrification
- In auto-catalytic systems, non-isothermal kinetic measurements are hampered by the confounding of thermal activation and increasing catalysis over time, but isothermal measurements are not hampered by a large initial transient.

FlexCy and Primaset® PT-30: FT-IR Cure Comparison

FlexCy

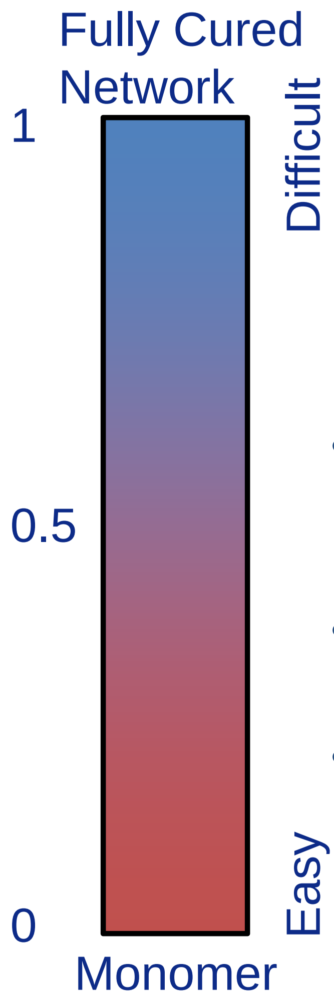


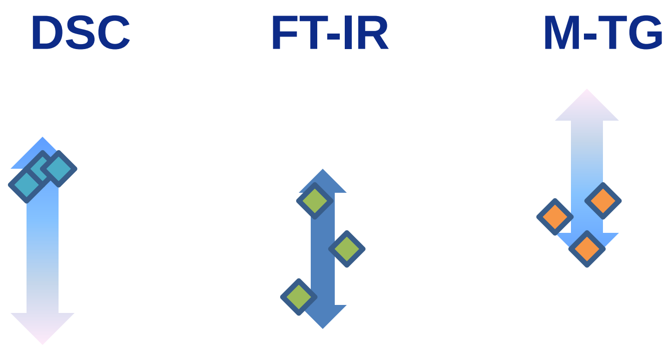
PT-30



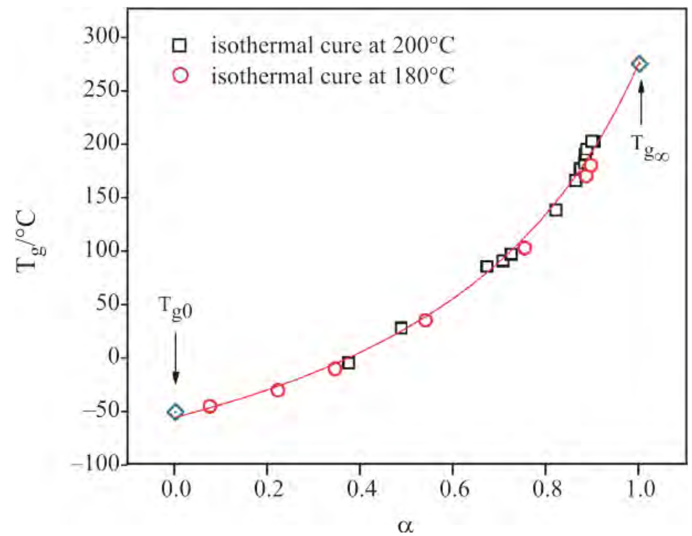
- FT-IR spectra are referenced to the phenyl peak at 1500 cm^{-1}
- Peaks near 2250 cm^{-1} signify uncured cyanate ester groups, those at 1360 cm^{-1} and 1550 cm^{-1} signify cyanurate rings (i.e., properly cured cyanate ester groups)
- FT-IR conversion estimates of 95% (FlexCy) and 80% (PT-30) are only approximate due to their dependence on the choice of reference peaks, baselines, and limits of integration, as well as the effects of changes in the solid-state structure during cure.

Measurements of Conversion in High-Temperature Thermosets





- **DSC**: High precision, but both full cure and maximum attainable cure give the same (lack of) signal
- **FT-IR**: Absolute bounds, but low quantitative accuracy and precision
- **Mechanical T_g** (DMA, etc.): Good precision, but samples can cure or degrade *in-situ*



An example of how Tg values can be converted to conversion values based on the diBenedetto equation (from X. Sheng, M. Akinc, and M. R. Kessler, *J. Therm. Anal. Calorim.* **2008**, 93, 77-85.) for EX-1510 dicyanate ester resin, for which T_g << T_{decomp}

- **Multiple techniques, when combined, can provide a reasonable estimate of conversion**

Conversion Measurements for FlexCy and PT-30

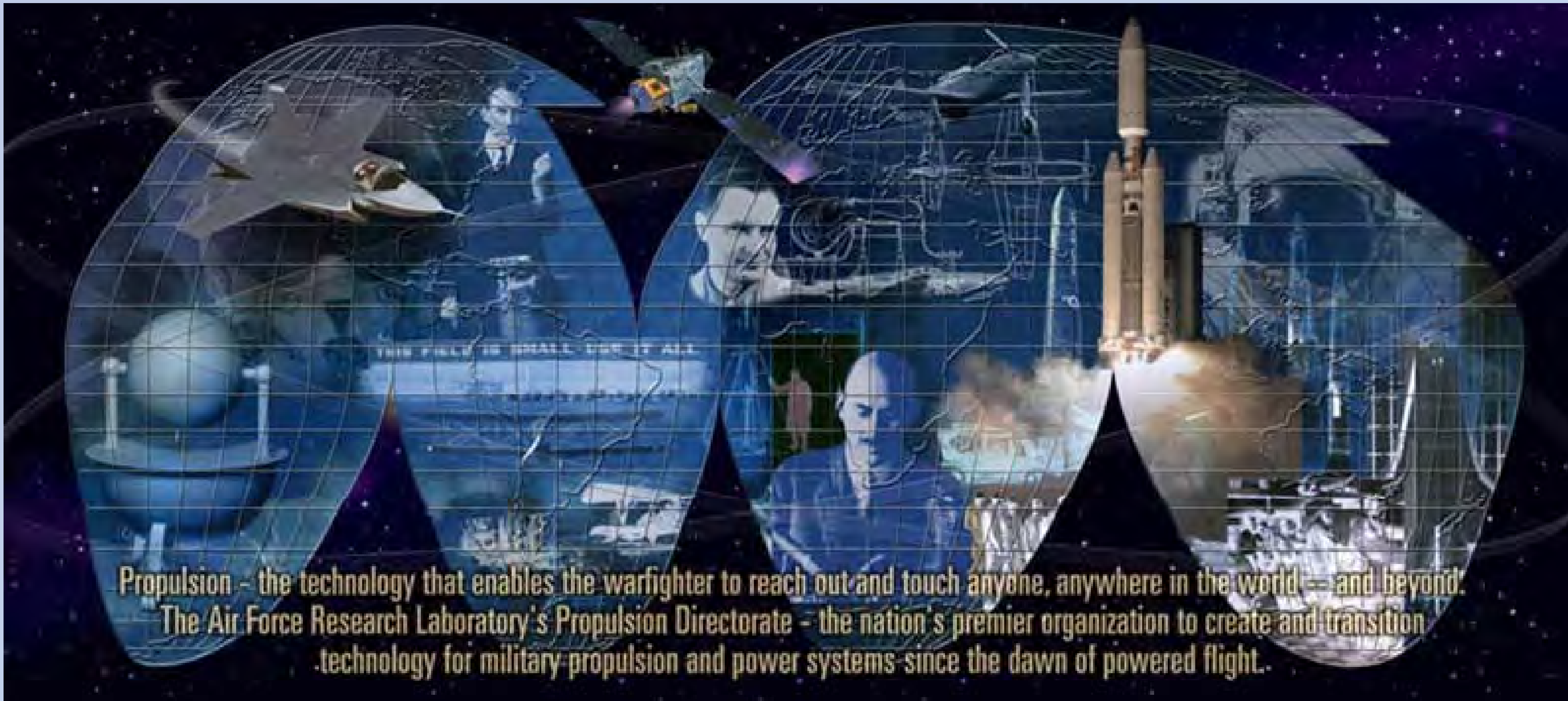
Material	Cure Temp. (°C)	Cure Time (hrs)	Tg via OTMA CTE (°C)	Tg via OTMA Loss Peak (°C)	Conver-sion via OTMA CTE	Conver-sion via OTMA Loss Peak	Conver-sion via FT-IR	Conver-sion via DSC
FlexCy-IPA	210	24	310	338	0.91	0.92	0.83	n/a
FlexCy-IPA	250	2	307	>352[a]	0.90	>0.94	0.82	n/a
FlexCy-IPA	290	0.5	>349[a]	>349[a]	>0.95	>0.94	0.94	<0.98
FlexCy-IPA[c]	210 / 290	24 / 0.5	302	351	0.89	0.94	n/a	n/a
FlexCy-EtOH	210	24	301	317	0.89	0.88	n/a	n/a
FlexCy-EtOH	250	2	327	>354[a]	0.93	>0.94	n/a	n/a
FlexCy-EtOH	290	0.5	301	>352[a]	0.89	>0.94	n/a	<0.98
PT-30	210	24	274	309	0.82	0.85	0.80	n/a
PT-30	250	2	309	>355[a]	0.88	>0.93	0.91	n/a
PT-30	290	0.5	327	>352[a]	0.91	>0.92	0.80	<0.99
PT-30[c]	210 / 290	24 / 0.5	314	>389[a]	0.89	>0.98	n/a	n/a

a. Run terminated due to sample decomposition prior to measurement of loss peak

- Under some cure conditions, FlexCy exhibits a higher T_g than PT-30, indicating a higher extent of cure was achieved
- Although all samples show >80% conversion, quantitative comparisons are difficult
- Loss modulus is more reliable than CTE for conversion determination via TMA

Conclusions

- The inclusion of a flexible core chemistry in cyanate esters confers benefits including lower activation energy, greater extent of cure under many cure conditions, and even higher maximum use temperatures in environments involving long-term water and short-term thermo-oxidative exposure
- For auto-catalytic cyanate esters, isothermal methods for measuring kinetics appear to offer fewer difficulties, in contrast to most non-autocatalytic systems for which non-isothermal kinetic measurements are often simpler
- Despite the difficulties, in general non-isothermal kinetic methods produced similar activation energy values for the cyanate esters studied
- Conversion tracking is best handled by a combination of methods, even so, achieving a precise quantitative estimate can be more difficult than expected



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